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(54) Title: AMPHOTERIC WATER-IN-OIL SELF-INVERTING POLYMER EMULSION (57) Abstract <p>An amphoteric water-in-oil self-inverting polymer emulsion is prepared which contains a copolymer of (1) a nonionic vinyl monomer and (2) an amphoteric vinyl monomer or a terpolymer of (1) a nonionic vinyl monomer, (2) an anionic vinyl monomer and (3) a cationic vinyl monomer in the aqueous phase, a hydrocarbon oil for the oil phase, a water-in-oil emulsifying agent and an inverting surfactant. An example of a copolymer is a copolymer of (1) a nonionic vinyl monomer such as acrylamide or methacrylamide and (2) an amphoteric vinyl monomer such as a reaction product of dimethylaminoethyl methacrylate and monochloroacetic acid. An example of a terpolymer is a terpolymer of (1) a nonionic vinyl monomer such as acrylamide or methacrylamide, (2) an anionic vinyl monomer such as sodium acrylate and (3) a cationic vinyl monomer such as a triethyl ammonium ethyl methacrylate methosulfate salt. The emulsion is useful in papermaking, treatment of sewage and industrial wastes, drilling muds and secondary and tertiary recovery of petroleum by water flooding.</p>		

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AMPHOTERIC WATER-IN-OIL SELF-INVERTING
POLYMER EMULSION

BACKGROUND OF THE INVENTION

1. Field of the Invention

This invention relates to amphoteric water-in-oil self-inverting polymer emulsions for use in paper-making, sewage treatment, drilling muds and petroleum recovery by water flooding.

2. Description of the Prior Art

Water-in-oil self-inverting polymer emulsions are used in commercial applications such as papermaking operations, treatment of sewage and industrial wastes, drilling muds, secondary and tertiary recovery of petroleum by water flooding.

Three types of polymeric emulsions, i.e., nonionic, cationic and anionic emulsions are known. Preparation of these emulsions is described in numerous patents. The internal phase of the emulsion is formed from a water solution of an ethylenic unsaturated monomer or comonomer such as (1) acrylamide, methacrylamide, (2) acrylic acid, methacrylic acid, (3) dimethylaminoethyl methacrylate, diethylaminoethyl methacrylate, dimethyl and diethylaminoethyl acrylate, allyl methacrylate and its quaternization products, (4) N-substituted methacrylamide and (5) vinyl sulfonate.

The external phase of the emulsion is formed using low HLB emulsifiers such as mono and diglycerides of fatty acids, sorbitan fatty acid monoesters, polyoxy-



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ethylene alcohols and the like dissolved in a solvent such as kerosene, xylene, toluene and chlorinated hydrocarbons.

5 A water-in-oil emulsion is produced by slowly adding the water phase to the oil phase under rapid agitation. The emulsion is homogenized to obtain the proper particle size and is then polymerized by one of the procedures described in the literature. After polymerization is completed, the final step is the
10 incorporation of an inverting agent, a high HLB surfactant, into the emulsion. The finished emulsion is uniform and disperses instantly by self-inversion in a water system. Water-in-oil emulsions and their uses have been described in the prior art. The following
15 patents are representative of the prior art.

U. S. Patent No. 3,284,393 - Vanderhoff et al, issued November 8, 1966, describes polymerization of vinyl monomer in the oil phase by forming a water-in-oil emulsion of the monomer in a hydrophobic liquid and
20 water with a water-in-oil emulsifier and then polymerizing the emulsion with a free radical catalyst to obtain a polymeric latex where the oil phase is the dispersion medium.

U. S. Patent No. 4,022,731 - Schmitt, issued
25 May 10, 1977, describes a self-inverting water-in-oil emulsion containing an acrylamide polymer in the aqueous phase, hydrocarbon oil, water-in-oil emulsifier and an inverting surfactant mixture containing two sulfo-succinates or one sulfosuccinate and an alkylphenol
30 ethoxylate.

U. S. Patent No. 4,022,736 - Schmitt, issued
May 10, 1977, describes a self-inverting water-in-oil
emulsion having a copolymer of acrylic acid in the
aqueous phase, hydrocarbon oil, water-in-oil emulsifier
35 and an inverting surfactant which is a fatty alcohol ethoxylate.



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U. S. Patent No. 4,077,930 - Lim et al, issued March 7, 1978, describes a stable, self-inverting water-in-oil emulsion obtained by emulsifying water soluble vinyl monomer in oil containing at least 20% emulsifier and a free radical catalyst and then polymerizing to obtain a stable polymer emulsion which can be inverted by adding water without any other reagent.

A common practice in plant operations such as in a paper mill is to change the charge in the system by switching from a nonionic polymer emulsion to a cationic or anionic polymer emulsion. In paper mill operations, the zeta potential should be determined to obtain optimum results. Choice of polymer emulsion depends on the type of charge in the previous operation and the type of charge required in the present operation. A change in charge is cumbersome and may require addition of varying quantities of a variety of polymers having different positive or negative charges.

SUMMARY OF THE INVENTION

An amphoteric water-in-oil self-inverting polymer emulsion is prepared which contains a copolymer of (1) a nonionic vinyl monomer and (2) an amphoteric vinyl monomer or a terpolymer of (1) a nonionic vinyl monomer, (2) an anionic vinyl monomer and (3) a cationic vinyl monomer in the aqueous phase, a hydrocarbon oil for the oil phase, a water-in-oil emulsifying agent and an inverting surfactant. This water-in-oil emulsion is prepared by dissolving the required monomers in the water phase, dissolving the emulsifying agent in the oil phase, emulsifying the water phase in the oil phase to prepare a water-in-oil emulsion, homogenizing the water-in-oil emulsion, polymerizing the monomers dissolved in the water phase of the water-in-oil emulsion to obtain the copolymer or terpolymer and then adding the self-



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inverting surfactant to obtain an amphoteric water-in-oil self-inverting water-in-oil emulsion. The emulsion is useful in papermaking, treatment of sewage and industrial wastes, drilling muds and secondary and tertiary recovery of petroleum by water flooding.

5 A useful copolymer is a copolymer of (1) a nonionic vinyl monomer such as acrylamide or methacrylamide and (2) an amphoteric vinyl monomer such as a reaction product of dimethylaminoethyl methacrylate and monochloroacetic acid. A useful terpolymer is a terpolymer of (1) a nonionic vinyl monomer such as acrylamide or methacrylamide, (2) an anionic vinyl monomer such as sodium acrylate and (3) a cationic vinyl monomer such as a triethyl ammonium ethyl methacrylate methosulfate salt.

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DETAILED DESCRIPTION

Most research on water-in-oil polymer emulsions has been with nonionic, anionic or cationic polymers. Amphoteric polymers have not been studied extensively so very little is known about them. Investigation of amphoteric polymer emulsions produced by this invention has shown that they have numerous advantages over nonionic, anionic and cationic polymer emulsions.

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For example, the anionic charge on an amphoteric polymer can be increased by addition of alkali and the cationic charge on an amphoteric polymer can be increased by addition of acid. The charge can be varied by small incremental alkali or acid additions. It is possible to change the charge in a system such as a paper mill operation by simple alkali or acid additions to an amphoteric polymer emulsion in the system. Use of an amphoteric polymer emulsion eliminates need for the variety of nonionic, anionic and cationic polymers which are now required to vary the charge in a system.

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In a copolymer, the molar ratio of amphoteric vinyl monomer to nonionic vinyl monomer in the copolymer may be varied over a wide range, i.e., about from 1% of the amphoteric vinyl monomer to about 99% nonionic vinyl monomer, e.g., up to 70% of amphoteric vinyl monomer and 30% of nonionic vinyl monomer. The preferred molar ratio is from about 10% to about 50% of the amphoteric vinyl monomer on a molar basis in a copolymer. Since a terpolymer contains a nonionic vinyl monomer, anionic vinyl monomer and cationic vinyl monomer, the anionic vinyl monomer and cationic vinyl monomer are considered to be equivalent to an amphoteric vinyl monomer and the above copolymer ratios are applicable.

Useful water soluble nonionic vinyl monomers include acrylamide, methacrylamide, allyl alcohol, 3-methylallyl alcohol, vinyl chloride, vinyl methyl ether, vinyl ethyl ether and the like.

Useful water soluble cationic vinyl monomers include

(1) N-substituted-(N'-dialkylaminoalkyl)acrylamides such as:

N-(diethylaminomethyl)acrylamide,
N-(diethylaminomethyl)methacrylamide,
N-(dimethylaminomethyl)acrylamide,
N-(dipropylaminomethyl)acrylamide,
N-(piperidylmethyl)acrylamide;

(2) Aminoalkylacrylates and dialkylaminoalkylacrylates such as:

Diethylaminopropylacrylate,
Dimethylaminoethylacrylate,
Dimethylaminopropylacrylate;

(3) Vinylpyridine;

(4) Diallylamines such as:

Diallylbenzylamine;
Diallylmethylamine,
Diallylethylamine;



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(5) Quaternaries such as:

Acrylamidopropylbenzyltrimethylammonium hydroxides,
N-methyl-vinylpyridinium chloride,
Diallyldimethylammonium chloride,
5 Diallyldiethylammonium chloride,
Acrylopropylbenzyltrimethylammonium hydroxide.

Quaternaries having at least one ethylenically unsaturated substituent may also be prepared using members of groups (1), (2), (3), (4) and the like.

10 Useful water soluble anionic vinyl monomers include acrylic acid, 1,2-dichloroacrylic acid, 2-methyl-cis-acrylic acid, 2-methyl-trans-acrylic acid, ethylene sulfonic acid, fumaric acid, chlorofumaric acid, methyl-fumaric acid, itaconic acid, maleic acid, dichloromaleic
15 acid, methylmaleic acid, methacrylic acid, styrene sulfonic acid, crotonic acid, their salts and the like.

Useful water soluble amphoteric vinyl monomers may be prepared by reacting any of the above cationic vinyl monomers with an anionic reactant such as chloro-
20 acetic acid, chlorosulfonic acid, bromoethanol sulfonic acid or the like.

The oil phase may be any inert hydrophobic liquid. A preferred group of organic liquids are the hydrocarbon liquids which include both aromatic and
25 aliphatic compounds. Hydrocarbon liquids such as benzene, xylene, toluene, mineral oil, mineral spirits, kerosene, naphtha and the like may be used.

Free radical yielding initiators useful as catalysts in polymerizing vinyl monomers, such as
30 benzoyl peroxide, lauroyl peroxide, 2,2'-azobis (isobutyronitrile), potassium persulfate and the like may be used in the polymerization, advantageously in amounts ranging between about 0.002 and about 0.2 percent by weight of the oil or aqueous monomer phase, depending
35 upon the solubility of the initiator. Polymerization can



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also be carried out using high energy irradiation such as high energy electrons from a Van de Graaff accelerator, ultraviolet irradiation or the like.

Water-in-oil emulsifying agents useful in the present invention may be blends of low HLB and high HLB surfactants having a final HLB of 7, preferably 4 to 5. Suitable blends may be prepared using emulsifying agents from the table below entitled, "Emulsifying Agent - Chemical Composition HLB (+)". Additional details on these agents may be found in the Atlas Chemical Industries bulletin, "General Characteristics of Atlas Surfactants", copyright 1963.

EMULSIFYING AGENT - CHEMICAL COMPOSITION HLB (+1)

Class 100 - Mono and Diglycerides

15	Mono and diglycerides from the glycerolysis of edible fats	3.2
	Mono and diglycerides of fat forming fatty acids	2.8
	Mono and diglycerides from the glycerolysis of edible fats	2.8
20	Mono and diglycerides from the glycerolysis of edible fats	2.8
	Mono and diglycerides from the glycerolysis of edible fats	3.5
25	Mono and diglycerides from the glycerolysis of edible fats	3.5
	Mono and diglycerides from the glycerolysis of edible fats or oils	3.5
	Mono and diglycerides from the glycerolysis of edible fats and Tween 80	5.2
30	Mono and diglycerides from the glycerolysis of edible fats and Tween 65	5.9
	Glycerol monostearate (acid-stable, self-emulsifying)	11.0



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EMULSIFYING AGENT - CHEMICAL COMPOSITIONHLB (+1)Class 200 - Sorbitan Fatty Acid Esters

	Sorbitan monooleate	4.3
	Sorbitan partial fatty esters	4.3
5	Sorbitan partial fatty esters	4.3
	Sorbitan monopalmitate	6.7
	Sorbitan monostearate	4.7
	Sorbitan monooleate	4.3
	Sorbitan sesquioleate	3.7
10	Sorbitan trioleate	1.8
	Sorbitan monopalmitate	6.7
	Sorbitan monostearate	4.7
	Sorbitan tristearate	2.1
	Sorbitan monooleate	4.3
15	Sorbitan trioleate	1.8
	Sorbitan monolaurate	8.6
	Sorbitan monolaurate	8.6

Class 300 - Polyoxyethylene Sorbitan

20	<u>Fatty Acid Esters</u>	
	Polyoxyethylene sorbitan esters of mixed fatty and resin acids	14.6
	Polyoxyethylene sorbitan esters of mixed fatty and resin acids	15.4
25	Polyoxyethylene (20) sorbitan monolaurate	16.7
	Polyoxyethylene (4) sorbitan monolaurate	13.3
	Polyoxyethylene (20) sorbitan monopalmitate	15.6
	Polyoxyethylene (20) sorbitan monostearate	14.9
	Polyoxyethylene (4) sorbitan monostearate	9.6
30	Polyoxyethylene (20) sorbitan tristearate	10.5
	Polyoxyethylene (20) sorbitan monooleate	15.0
	Polyoxyethylene (5) sorbitan monooleate	10.0
	Polyoxyethylene (20) sorbitan trioleate	11.0



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EMULSIFYING AGENT - CHEMICAL COMPOSITION HLB (± 1)

Class 400 - Polyoxyethylene Sorbitol

Esters

	Polyoxyethylene sorbitol beeswax derivative	5
5	Polyoxyethylene sorbitol beeswax derivative	5
	Polyoxyethylene sorbitol oleate-laurate	13.2
	Polyoxyethylene sorbitol oleate	9.2
	Polyoxyethylene sorbitol oleate	11.4
	Polyoxyethylene sorbitol tall oil	10.7
10	Polyoxyethylene sorbitol tall oil	9.7
	Polyoxyethylene sorbitol laurate	11.5
	Polyoxyethylene sorbitol hexa-oleate	10.2
	Polyoxyethylene sorbitol hexa-oleate	11.4
	Polyoxyethylene sorbitol oleate	10.2
15	Polyoxyethylene sorbitol esters of mixed fatty and resin acids	8.6
	Polyoxyethylene sorbitol lanolin derivative	14
	Polyoxyethylene sorbitol lanolin derivative	16
	Polyoxyethylene sorbitol tallow esters	9.6

20 Class 500 - Polyoxyethylene Acids

	Polyoxyethylene (8) stearate	11.1
	Polyoxyethylene (40) stearate	16.9
	Polyoxyethylene (40) stearate	16.9
	Polyoxyethylene (50) stearate	17.9
25	Polyoxyethylene esters of mixed fatty and resin acids	13.8
	Polyoxyethylene (20) palmitate	15.5
	Polyoxyethylene (8) laurate	12.8



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EMULSIFYING AGENT - CHEMICAL COMPOSITION HLB (+1)

Class 600 - Polyoxyethylene Alcohols

	Polyoxyethylene (2) cetyl ether	5.3
	Polyoxyethylene (2) stearyl ether	4.9
5	Polyoxyethylene (2) oleyl ether	4.9
	Polyoxyethylene (4) lauryl ether	9.7
	Polyoxyethylene (23) lauryl ether	16.9
	Polyoxyethylene (10) cetyl ether	12.9
	Polyoxyethylene (20) cetyl ether	15.7
10	Polyoxyethylene (10) stearyl ether	12.4
	Polyoxyethylene (20) stearyl ether	15.3
	Polyoxyethylene (10) oleyl ether	12.4
	Polyoxyethylene (20) oleyl ether	15.3
	Polyoxyethylene (12) tridecyl ether	14.5
15	Polyoxyethylene (15) tridecyl ether	15.4
	Polyoxyethylene (12) tridecyl ether urea complex	14.5
	Polyoxyethylene (6) tridecyl ether	11.4

Class 700 - Polyoxyethylene Adducts

20	<u>Not Otherwise Classified</u>	
	Polyoxyethylene fatty glyceride	16.0
	Polyoxyethylene fatty glyceride	10.8
	Polyoxyethylene fatty glyceride	17.5
	Polyoxyethylene glyceride ester	18.1
25	Polyoxyethylene lanolin derivative	11.0
	Polyoxyethylene lanolin derivative	17.0
	Polyoxyethylene (25) oxypropylene monostearate	16.0
	Polyoxyethylene alkyl amine	15.5



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Any inverting surfactant or inverting surfactant mixture described in the prior art may be used. These surfactants include surfactant mixtures having a HLB of about 12 to about 20. Surfactant mixtures such as sodium bis(2-ethylhexyl)sulfosuccinate and sodium bis(C₁₁-C₁₅ alkyl) sulfosuccinate or ethoxylated octyl or nonyl phenol may be used. These mixtures are described in U.S. Patent No. 4,022,731 - Schmitt, issued May 10, 1977, whose teachings on inverting surfactant mixtures are incorporated by reference herein. Preferred inverting surfactants include the condensation product of one mole of nonyl phenol and nine moles of ethylene oxide as well as its mixtures with sodium bis(2-ethylhexyl)sulfosuccinate.

The amphoteric water-in-oil self-inverting polymer emulsion is prepared by (1) dissolving (a) a water soluble nonionic vinyl monomer and a water soluble amphoteric vinyl monomer or (b) a water soluble nonionic vinyl monomer, a water soluble anionic vinyl monomer and a cationic vinyl monomer in water to form an aqueous phase, dissolving an emulsifying agent in a hydrophobic liquid to form an oil phase, emulsifying the aqueous phase in the oil phase to prepare a water-in-oil emulsion, homogenizing the water-in-oil emulsion, polymerizing under polymerization conditions the monomers dissolved in the water phase of the water-in-oil emulsion using a free radical yielding initiator as a catalyst to obtain the copolymer of (a) or terpolymer of (b) and then adding a self-inverting surfactant to an amphoteric water-in-oil emulsion.

Amphoteric water-in-oil self-inverting polymer emulsions may be prepared using the Indicated and Preferred parts by weight (pbw) ranges of the following components:



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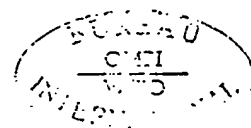
	Indicated (pbw)	Preferred (pbw)
polymer	10 - 50	20 - 35
water	10 - 50	15 - 40
5 hydrophobic liquid	5 - 50	10 - 40
emulsifying agent	2 - 25	3 - 10
free radical yielding initiator	0.01 - 0.25	0.02 - 0.1
inverting surfactant	1 - 15	3 - 10

- 10 The polymer may be a copolymer or terpolymer prepared using the Indicated or Preferred parts by weight (pbw) of nonionic vinyl monomer with the appropriate monomer or monomers and monomer ratio.

	Indicated (pbw)	Preferred (pbw)
15 nonionic vinyl monomer	30 - 99	50 - 90
amphoteric vinyl monomer	1 - 70	10 - 50
anionic vinyl monomer	1 - 35	5 - 25
20 cationic vinyl monomer	1 - 35	5 - 25
copolymer (monomer ratio)	99:1 - 3:7	9:1 - 1:1
terpolymer (monomer ratio)	48:1:1 - 3:3.5:3.5	9:0.5:0.5-5:2.5:2.5

- 25 The polymer may be prepared by polymerizing the appropriate monomers at from about 30 to about 70°C over about 2 to about 20 hours with the preferred temperature range being from about 35 to about 65°C and preferred time range being over about 4 to about 10 hours.

- 30 The amphoteric polymers present in the emulsions of this invention are versatile polyelectrolytes. They are polyampholytes having both anionic and cationic substituents. The charge on these polymeric ampholytes can be changed by addition of alkali or acid. Where a



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specific charge on the polyelectrolyte is required, the charge on the polymer may be "fine tuned" by small alkali or acid additions. These polyampholyte emulsions are useful in papermaking, treatment of sewage and industrial wastes, drilling muds and secondary, tertiary and enhanced oil recovery by water flooding.

In papermaking, the ease with which water drains from stock on a paper machine "wire" and amount of water retained in the wet web as it passes to and through the presses affects both speed of the machine and quality of the paper. Use of these amphoteric polymer emulsions in papermaking as drainage aids improves drainage rates and provides other benefits. Emulsion performance may be optimized by acidification or alkalization.

These amphoteric polymer emulsions are useful in drilling muds as well as in secondary, tertiary and enhanced oil recovery (EOR). Since the charge on the polymer can be varied over a wide range, the charge can be easily changed where a specific electrical charge is required in oil production problems. These emulsions are useful in high water oil ratio (WOR), erratic channeling, channel sealing, sand and clay mobility problems.

For a fuller understanding of the nature and advantages of this invention, reference may be made to the following examples. These examples are given merely to illustrate the invention and are not to be construed in a limiting sense. All quantities, proportions and percentages are by weight and all references to temperature are °C unless otherwise indicated.



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EXAMPLE I

This example demonstrates preparation of an amphoteric water-in-oil self-inverting polymer emulsion using the following procedure:

(A) A total of 50.0 parts by weight of
5 dimethylaminoethyl methacrylate (0.318 mole) was charged to a reactor and cooled to a temperature of 8°C. Then 30.0 parts by weight of monochloroacetic acid (0.318 mole) was added under stirring and cooling until a uniform viscous liquid was formed. Temperature of the
10 reaction mixture rose to a maximum of 22°C. Molar ratio of the reactants was 1:1. An aqueous solution of a sample of the reaction product, a monomer, formed a heavy precipitate when treated with aqueous silver nitrate solution showing the presence of a quaternary compound.

15 (B) A total of 250.0 parts by weight of aqueous 52% acrylamide solution (1.83 mole), 0.2 parts by weight of a 34% aqueous diethylenetriamine pentacetic sodium salt solution and 90.0 parts by weight of tap water were charged to the reactor containing the
20 quaternary compound prepared in (A) and stirred to form a uniform solution, the water phase for the emulsion. The water phase, an aqueous solution of comonomers, had a pH of 5.8.

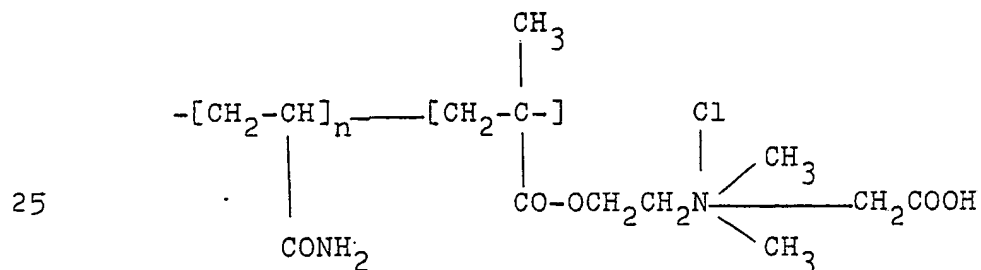
(C) Utilizing a separate reactor, 180.0 parts
25 by weight of kerosene and a mixture of 32.0 parts by weight of oleyl mono glyceride and 6.0 parts by weight of stearyl mono glyceride as the emulsifying agent were mixed and heated to 40°C to obtain a uniform solution, the oil phase for the emulsion.

30 (D) The water phase from (B) was added slowly with rapid agitation to the oil phase in the reactor from (C) to obtain a water-in-oil emulsion. After emulsification, the water-in-oil emulsion was homogenized in a Waring blender and transferred to a
35 polymerization reactor.



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(E) A total of 500.0 parts by weight of the water-in-oil emulsion was sparged with nitrogen at room temperature for 1/2 hour, then 0.4 parts by weight of 2,2'-azo(bis)isobutyronitrile dissolved in 2.0 parts by weight of acetone was added and the mixture heated slowly to 40°C under constant sparge with nitrogen. Temperature of polymerization was maintained at 40°C for 3 hours and then was raised to 42°C where a vigorous exothermic reaction raised the temperature to 60°C over 30 minutes. The polymerization mixture was then agitated for an additional 30 minutes at 60°C and 40.0 parts by weight of an ethoxylated (9 E.O.) nonyl phenol was added as the inverting surfactant and the viscous solution was agitated for an additional 30 minutes. During polymerization, appearance of the water-in-oil emulsion changed gradually from milky to glassy and then to semi-transparent hazy. After addition of the inverting surfactant, the emulsion had the appearance of a viscous, gray, hazy, uniform liquid. The polymer molecular weight unit and formula were as follows:



where n is 5.75.

The calculated molecular weight unit was 660.



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Following data summarize the properties of the emulsion:

	Solids:	42%, constant weight, moisture balance
5	Active content:	30.4%
	Viscosity as is:	2640 cps, Brookfield Spindle No. 3/30 rpm, 24°C
	Viscosity 1% solution:	340 cps Brookfield Spindle No. 2/30, 24°C
10	pH 1% solution:	6.0
	Flash point:	150°F
	Freeze-thaw test:	Recovers to original appearance after freezing to 0°F and
15	Heat stability test:	thawing at room temperature, remains liquid after 3 days at 50°C
	Flocculation test-acid:	67% improvement in drainage time
20	Flocculation test-alkaline:	56% improvement in drainage time
	Cationic activity-acid:	10.56%
	Anionic activity-alkaline:	15.84%
	Intrinsic viscosity:	27
25	Molecular weight:	10.9 million
	Huggins constant:	0.52

EXAMPLE II

This example demonstrates preparation of an amphoteric water-in-oil self-inverting polymer emulsion using the following procedure:

- 30 (A) Utilizing a reactor as a mixer, 137.0 parts
of 52% acrylamide aqueous solution (1.0 mole), 100.0
parts tap water, 0.2 parts by weight of a 34% diethylene-



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5 triamine pentacetic sodium salt water solution, 18.0
parts by weight of acrylic acid (0.25 mole), 20.0
parts 50% sodium hydroxide aqueous solution (0.25 mole)
were charged in the above order and mixed together to
obtain a uniform solution having a pH of 7.8.

10 (B) Then, 88.0 parts by weight of a 80% active
aqueous solution containing 0.25 mole of a quaternization
product obtained by reaction of dimethylaminoethyl
methacrylate and dimethyl sulfate was charged to (A) in
the reactor and mixed together to obtain a uniform
solution having a pH of 7.4, the water phase (B).

15 (C) In a separate reactor, 150.0 parts by
weight of kerosene was charged and then 30.0 parts by
weight of oleyl monoglyceride and 6.0 parts by weight
of stearyl monoglyceride were added. The charge was
heated to 40°C and mixed to obtain a uniform solution,
the oil phase.

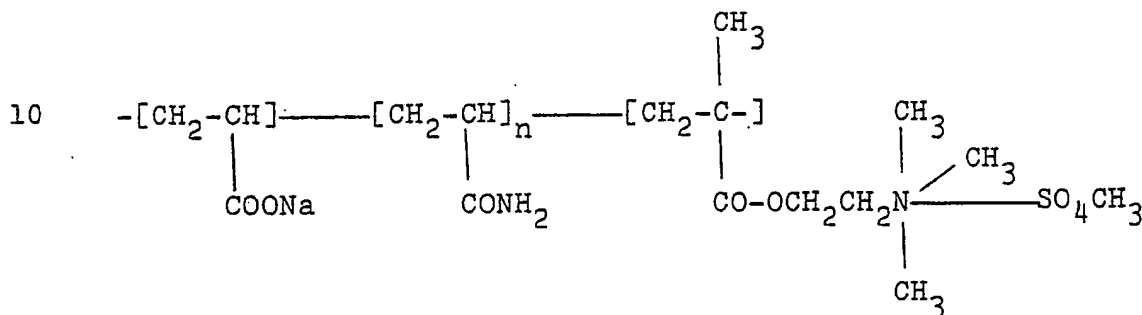
20 (D) The water phase from (B) was then added
slowly under rapid agitation to the oil phase from (C)
to obtain a water-in-oil emulsion of the monomers. The
resulting water-in-oil emulsion was homogenized and
transferred to a polymerization reactor.

25 (E) The emulsion representing 500.0 parts by
weight was sparged with nitrogen at room temperature
for 1/2 hour in the polymerization reactor, then 0.6
parts by weight 2,2'-azo(bis)isobutyronitrile, dissolved
in 3.0 parts by weight acetone, was added and the
resulting mixture heated slowly to 40°C under constant
sparge with nitrogen. Temperature of the polymerization
30 mixture was maintained at 40°C for 3 hours and then
raised to 43°C where an exothermic reaction increased
the polymerization temperature to 56°C over 1 hour.
The polymerization mixture was heated to 60°C and 40.0
parts by weight of an ethoxylated (9 E.O.) nonyl phenol
35 followed by 7.5 parts by weight of sodium bis(ethylhexyl)



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sulfosuccinate were added as an inverting surfactant mixture to the polymer and the emulsion was agitated for an additional 1/2 hour. Properties of the polymer emulsion are summarized after Example III. The polymer
 5 molecular weight unit and formula were as follows:



15 where n is 4.

The calculated molecular weight unit was 661.

EXAMPLE III

This example demonstrates preparation of an amphoteric water-in-oil self-inverting polymer emulsion using the following procedure:

20 (A) Utilizing a reactor as a mixer, 164.4 parts by weight of 52% acrylamide aqueous solution (1.2 mole), 120.0 parts by weight of tap water, 0.2 parts by weight of a 34% diethylenetriamine pentacetic sodium salt aqueous solution, 10.8 parts by weight of acrylic acid
 25 (0.15 mole), 12.0 parts by weight of 50% sodium hydroxide aqueous solution (0.15 mole) were charged in the above order to the reactor and mixed to obtain a solution having a pH of 6.2.

30 (B) Then 52.8 parts by weight of a 80% active dimethyl sulfate quaternary of dimethylaminoethyl methacrylate (0.15 mole) was charged to (A) in the reactor and mixed to obtain a uniform solution having a pH of 6.6, the water phase.

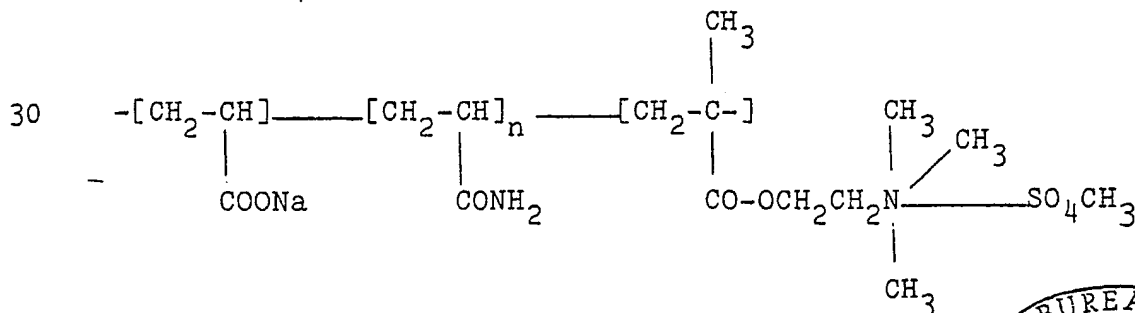


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(C) In a separate reactor, 168.0 parts by weight of kerosene, 32.4 parts by weight of oleyl monoglyceride and 6.0 parts by weight of stearyl monoglyceride were mixed together and heated to 40°C to obtain a uniform solution, the oil phase.

(D) Then the water phase from (B) was added slowly to the oil phase from (C) under rapid agitation to obtain a water-in-oil emulsion which was then homogenized and transferred to a polymerization reactor.

(E) The emulsion representing 500.0 parts by weight of the emulsion from (D) was sparged with nitrogen for 1/2 hour at 27°C temperature in the polymerization reactor, then 0.54 parts by weight of 2,2'-azo(bis) isobutyronitrile dissolved in 3.0 parts by weight of acetone were added and mixed. The polymerization mixture was heated to 40°C and maintained at 40°C for 3 hours. Then the temperature was raised to 42°C where a mild exothermic reaction raised the temperature to 48°C over 1/2 hour. The polymerization mixture was then heated to 60°C. A mixture of 30.0 parts by weight of an ethoxylated (9 E.O.) nonyl phenol and 7.5 parts of sodium bis(ethylhexyl)sulfosuccinate were added as an inverting surfactant mixture to the polymer emulsion and the emulsion was agitated for an additional 1/2 hour. The polymer molecular weight unit and formula were as follows:



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where n is 8.

The calculated molecular weight unit was 945. Properties of the polymer emulsion together with the emulsion from Example II are given below.

5 Following data summarize the properties of the emulsions from Example II and Example III.

	<u>Example II</u>	<u>Example III</u>
10 Solids	41.3%	36.5%
Active content	27.4%	23.2%
Viscosity as is	2,050 cps 3/30 24°C	1,120 cps 3/30 24°C
Viscosity 1% solution - acid	6 cps 2/30 24°C	6 cps 2/30 24°C
15 Viscosity 1% solution - alkaline	48 cps 2/30 24°C	40 cps 2/30 24°C
pH 1% solution as is	7.65	7.65
Freeze-thaw test	passes	passes
Heat stability test	passes	passes
Flocculation test - acid		
20 Improvement in drain time	37%	45%
Flocculation test - alkaline, improvement in drain time	58%	64%
Cationic activity - acid	7.93%	7.56%
25 Anionic activity - alkaline	8.32%	3.97%

EXAMPLE IV

30 This example describes determination of percent anionic and cationic activity in amphoteric polymer emulsion. This method determines the percent active ingredients in an anionic/or cationic activity titrating the emulsion with a cationic or anionic agent. The following procedure was used in this determination:



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APPARATUS

25 ml Burette with 0.05 ml graduations
100 ml Volumetric Flask
1000 ml Volumetric Flask
10 ml Bulb Pipette
5 15 ml Bulb Pipette
25 ml Bulb Pipette
250 Glass Stoppered Erlenmeyer Flasks

REAGENTS

10 Chloroform, reagent grade
Duponol[®] Solution, 0.004 mole
Dissolve 1.152 g of Duponol[®] C (100%
active) in distilled water and dilute
to 1 liter in a volumetric flask
Hyamine[®] Solution, 0.004 mole
15 Dissolve 1.815 g (based on 98.8% assay)
Hyamine in distilled water and dilute
to 1 liter in a volumetric flask.
Methylene Blue Indicator
Dissolve 0.030 g methylene blue, reagent
20 grade, and 50 g of anhydrous sodium
sulfate, reagent grade, in 500 mls of
distilled water. Add 6.5 mls of
sulfuric acid (96% reagent grade) and
dilute to 1000 mls with distilled
25 water. Shake well.
Sodium Sulfate, reagent grade
Sulfuric Acid, 96% reagent grade

PROCEDURE

30 a. Weigh between 0.2 - 0.5 g of the sample
to be analyzed to the nearest 0.0001 g.
Transfer to a 100 ml volumetric flask
with distilled water, dissolve and
dilute to the mark with distilled
water.



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- b. Pipette 10 mls of the sample solution prepared in "a" into a 250 ml glass stoppered Erlenmeyer flask (or 100 ml Nessler Tube).
- 5 c. Pipette 25 mls of methylene blue indicator solution and 15 mls of chloroform into the flask. If the upper layer is colorless and the lower layer blue, titrate with the cationic reagent (Hyamine, 0.004 mole). A
- 10 blue upper layer and colorless lower layer is indicative of a cationic, and the titration should be made with the anionic solution (Duponol C, 0.004 mole).
- 15 d. Titrate with the appropriate solution by running in 5 mls, shaking for 30 seconds and then adding 1 ml of titrate at a time and shaking the flask for 30 seconds after each addition.
- 20 e. When signs of the approaching end point appear, reduce the additions to 0.5 ml (more rapid separation of the temporary emulsification is an indication of the approaching end point).
- 25 f. In the Hyamine titration, the water will begin to turn blue near the end point. Add the Hyamine, 0.004 mole a drop at a time, shake for 30 seconds after each addition, and wait for 60 seconds until
- 30 the aqueous layer is clear and appears as blue as the chloroform layer. The comparison is made by placing the flask in reflected light, and obstructing one's view of the interface with a
- 35 stirring rod. The titration with



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5 Duponol C, 0.004 mole for a cationic sample is carried on exactly the same as that for the Hyamine, 0.004 mole except the chloroform layer will become bluer with addition of Duponol C. The end point is also indicated by equal intensity of blue color in the upper and lower layers.

10 CALCULATIONS % Anionic = $\frac{\text{mls Hyamine} \times 0.004 \times \text{M.W.}}{\text{original sample wt}}$
 % Cationic = $\frac{\text{mls Duponol C} \times 0.004 \times \text{M.W.}}{\text{original sample wt}}$

15 Cationizing and Anionizing Amphoteric Emulsion Polymers of Example I

Conversion to a cationic polymer

 To a 50.0 g sample of the polymer emulsion of Example I was added under good stirring 2.3 g sulfuric acid 50%. A 0.25 g sample of the acidified material was dissolved in 100 ml distilled water.

Conversion to a anionic polymer

25 To a 50.0 g sample of the polymer emulsion of Example I was added 1.8 g 50% sodium hydroxide aqueous solution under good stirring. A 0.5 g sample of the alkalized material was dissolved in 100 ml distilled water.

Example II and Example III

Conversion to a cationic polymer

30 A 1.0 g sample of the polymer emulsion of Example II or III was dissolved in 100 ml distilled water and 0.55 g of 50% sulfuric acid solution was added under stirring.

Conversion to an anionic polymer

35 A 1.0 g sample of the polymer emulsion of Example II or III was dissolved in 100 ml distilled water and 1.0 g



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of 50% sodium hydroxide solution was added under stirring.

The six 100 ml solutions of the samples of the cationic and anionic polymer emulsions prepared above were titrated according to the procedure for determination of % activity.

	<u>Duponol C</u>	<u>Hyamine</u>
Example I		
Acidified polymer	1.0 ml	
Alkalinized polymer		3.0 ml
10 Example II		
Acidified polymer	3.0 ml	
Alkalinized polymer		4.0 ml
Example III		
Acidified polymer	2.0 ml	
15 Alkalinized polymer		1.5 ml
<u>Cationic activity</u>		
Example I	$\frac{1.0 \times 0.004 \times 660}{0.25}$	= 10.56%
Example II	$\frac{3.0 \times 0.004 \times 661}{1.0}$	= 7.93%
20 Example III	$\frac{2.0 \times 0.004 \times 945}{1.0}$	= 7.56%
<u>Anionic activity</u>		
Example I	$\frac{3.0 \times 0.004 \times 660}{0.5}$	= 15.84%
25 Example II	$\frac{4.0 \times 0.004 \times 661}{1.0}$	= 10.57%
Example III	$\frac{1.5 \times 0.004 \times 945}{1.0}$	= 5.67%



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EXAMPLE V

This example describes drainage tests using amphoteric polymer emulsions from Examples I, II and III after acid or alkaline treatment with repulped newsprint. The newsprint samples containing Example I emulsion had
5 been treated with 2% alum on a dry pulp basis while the newsprint samples containing Examples II and III emulsions were also treated with 2.6% alum on a dry pulp basis.

The drainage time tester was a graduated plastic cylinder about 14" long with an inside diameter of 2" having a plug for each and attached to a light chain. The
10 top plug was fitted with a short plastic tube which could be covered by the forefinger to hold the furnish in the tube after the bottom plug had been removed. The bottom plug was placed in the tester.

Waste newsprint at 2% consistency was beaten in a Noble and Wood Beater to approximately 400 C.S.F. (Canadian Standard Freeness). A 1050 ml sample of the waste newsprint pulp was diluted with 6000 ml of water to
15 obtain 0.3% consistency furnish and was kept agitated during the entire screening process.
20

The tester was filled with 0.3% furnish to the zero line so that the tester contained 500 ml of furnish, i.e., 1.50 g of dry fiber.

Samples of amphoteric polymer emulsions from Examples I, II and III after acid or alkaine treatments were diluted to 0.05% solids so that 1.50 ml of diluted
25 solution containing 0.05% solids per 1.50 g of dry fiber was equivalent to 1 lb per ton (pound of polymer per ton of dry paper).

Utilizing a 3 ml hypodermic syringe, 1.50 ml of the diluted polymer solution was injected into the furnish in the tester. Then the amounts of alum on a
30 dry pulp basis shown above were added. The top plug was placed securely in position on the tester and the tube connected to the top plug was securely covered with
35



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the forefinger to close the tubular opening.

While the tubular opening was securely covered with the forefinger, the tester was then slowly inverted (180° angle) and returned to the upright position ten times without shaking. After the tenth inversion, the tester was returned to the upright position and the bottom plug removed with the free hand.

A predetermined drainage volume of 200 ml was chosen. With the stop watch in one hand and the tester in the other hand with the forefinger covering the tubular opening, the forefinger was removed and the stop watch started to measure the time required to drain a volume of 200 ml. As soon as the drainage volume was 200 ml, the stop watch was stopped and the elapsed time recorded. The following results were obtained with the emulsions from Examples I, II and III.

	<u>Sample</u>	<u>Treatment</u>	<u>Drainage Time for 200 ml Volume Seconds</u>
20	Blank		37.5
	Example I		
		Acid	12.3
		Alkaline	16.5
	Blank		35.0
25	Example II		
		Acid	22.0
		Alkaline	14.5
	Blank		35.0
	Example III		
30		Acid	14.2
		Alkaline	12.5

The amphoteric polymer emulsion may be used in the following applications.



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In pulp and papermaking processes, addition of an effective amount of the amphoteric polymer emulsion to pulp improves drainage of the pulp. From about 0.005% to about 0.5% by weight of the emulsion may be added based on the weight of dry pulp.

In secondary and tertiary recovery of petroleum by water flooding, addition of an effective amount of the amphoteric polymer emulsion to the water flood improves recovery of petroleum. From about 0.005% to about 1.0% by weight of the emulsion may be added based on the weight of water in the flood.

In treatment of sewage and industrial waste, addition of an effective amount of the amphoteric polymer emulsion to aqueous waste improves flocculation of suspended solids in aqueous suspension. From about 0.01% to about 0.5% by weight of the emulsion may be added based on the weight of the suspension.

In treatment of drilling muds for use in petroleum exploitation, an effective amount of the amphoteric polymer emulsion is added to control viscosity of the mud during drilling. The emulsion may be used to reduce or increase viscosity of the mud. From about 0.01% to about 1.0% by weight of the emulsion may be added based on the weight of mud.

While the invention as been described with reference to certain specific embodiments thereof, it is understood that it is not to be so limited since alterations and changes may be made therein which are within the full and intended scope of the appended claims.



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WHAT IS CLAIMED IS:

1. An amphoteric water-in-oil self-inverting polymer emulsion comprising

(A) from about 10 to about 50 parts by weight of a polymer selected from the group consisting of

-(1) a copolymer having from about 30 to about 99 parts by weight of a water soluble nonionic vinyl monomer and from about 1 to about 70 parts by weight of a water soluble amphoteric vinyl monomer, and

(2) a terpolymer having from about 30 to 98 parts by weight of a water soluble nonionic vinyl monomer, from about 1 to about 35 parts by weight of a water soluble anionic vinyl monomer and from about 1 to about 35 parts by weight of a water soluble cationic vinyl monomer,

(B) from about 10 to about 50 parts by weight of water,

(C) from about 5 to about 50 parts by weight of a hydrophobic liquid,

(D) from about 2 to about 25 parts by weight of a water-in-oil emulsifying agent, and

(E) from about 1 to about 15 parts by weight of an inverting surfactant

wherein the polymer is in the aqueous phase.



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2. The amphoteric polymer emulsion of claim 1 wherein there is present in the polymer, a water soluble nonionic vinyl monomer selected from the group consisting of acrylamide, methacrylamide, allyl alcohol, 3-methylallyl alcohol, vinyl chloride, vinyl methyl ether and vinyl ethyl ether.
3. The amphoteric polymer emulsion of claim 1 wherein there is present in the polymer, a water soluble nonionic vinyl monomer selected from the group consisting of acrylamide and methacrylamide.
4. The composition of claim 1 wherein there is present in the polymer, a water soluble cationic vinyl monomer selected from the group consisting of N-substituted-(N'-dialkylaminoalkyl)acrylamide, aminoalkylacrylate, dialkylaminoalkylacrylate, vinylpyridine, diallylalkylamine and quaternary having at least one ethylenically unsaturated substituent.
5. The composition of claim 1 wherein there is present in the polymer, a water soluble cationic vinyl monomer selected from the group consisting of N-substituted-(N'-dialkylaminoalkyl)acrylamide and aminoalkylacrylate.
6. The composition of claim 1 wherein there is present in the polymer, a water soluble anionic vinyl monomer selected from the group consisting of acrylic acid, 1,2-dichloroacrylic acid, 2-methylacrylic acid, ethylene sulfonic acid, fumaric acid, chlorofumaric acid, methylfumaric acid, itaconic acid, maleic acid, dichloromaleic acid, methylmaleic acid, methacrylic acid, styrene sulfonic acid, crotonic acid and salt thereof.



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7. The composition of claim 1 wherein there is present in the polymer, an amphoteric water soluble vinyl monomer which is a reaction product of a cationic water soluble vinyl monomer selected from the group consisting of N-substituted-(N'dialkylaminoalkyl) acrylamide, aminoalkylacrylate, dialkylaminoalkyl-acrylate, vinylpyridine, diallylalkylamine and a quaternary having at least one ethylenically unsaturated substituent with an anionic reactant selected from the group consisting of chloroacetic acid, chlorosulfonic acid and bromoethanol sulfonic acid.

8. The amphoteric polymer emulsion of claim 1 wherein the polymer is a copolymer of acrylamide and an amphoteric vinyl monomeric reaction product of dimethyl-aminoethyl methacrylate and monochloroacetic acid.

9. The amphoteric polymer emulsion of claim 1 wherein the polymer is a terpolymer of acrylamide, acrylic acid and a quaternization vinyl monomeric reaction product of dimethylaminoethyl methacrylate and dimethyl sulfate.

10. The method of preparing the amphoteric polymer emulsion of claim 1 comprising

(A) forming a water-in-oil emulsion of

(1) from about 10 to about 50 parts by weight of a monomer mixture selected from the group consisting of

(a) from about 30 to about 99 parts by weight of a water soluble nonionic vinyl monomer and from about 1 to about 70 parts by weight of



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- a water soluble amphoteric vinyl monomer to form an amphoteric copolymer, and
- (b) from about 30 to 98 parts by weight of a water soluble nonionic vinyl monomer, from about 1 to about 35 parts by weight of a water soluble anionic vinyl monomer and from about 1 to about 35 parts by weight of a water soluble cationic vinyl monomer to form an amphoteric terpolymer,
- (2) from about 10 to about 50 parts by weight of water,
- (3) from about 5 to about 50 parts by weight of a hydrophobic liquid,
- (4) from about 2 to about 25 parts by weight of a water-in-oil emulsifying agent, and
- (5) an effective amount of a free radical yielding initiator to polymerize the monomer mixture,
- (B) polymerizing the monomer mixture under free radical polymerizing conditions to form a water-in-oil emulsion which contains finely dispersed particles of the amphoteric polymer, and
- (C) adding to the oil-in-water emulsion from about 1 to about 15 parts by weight of an inverting surfactant.



11. The method of claim 10 wherein the monomer mixture is acrylamide and an amphoteric vinyl monomer reaction product of dimethylaminoethyl methacrylate and monochloroacetic acid.

12. The method of claim 10 wherein the monomer mixture is acrylamide, acrylic acid and a quaternization vinyl monomeric reaction product of dimethylaminoethyl methacrylate and dimethyl sulfate.

13. In pulp and papermaking processes, the improvement which comprises adding to pulp an effective amount of the amphoteric polymer emulsion of claim 1 to improve drainage of the pulp.

14. In secondary and tertiary recovery of petroleum by water flooding processes, the improvement which comprises adding to the water flood an effective amount of the amphoteric polymer emulsion of claim 1 to improve recovery of petroleum.

15. In treatment of sewage and industrial waste by flocculation of suspended solids in the waste, the improvement which comprises adding to the aqueous waste an effective amount of the amphoteric polymer emulsion of claim 1 to improve flocculation of suspended solids from the waste.

16. In treatment of drilling muds for use in petroleum exploitation, the improvement which comprises adding to the mud an effective amount of the amphoteric polymer emulsion of claim 1 to control viscosity of the mud during drilling.



INTERNATIONAL SEARCH REPORT

International Application No

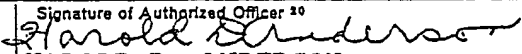
PCT/US80/01352

I. CLASSIFICATION OF SUBJECT MATTER (If several classification symbols apply, indicate all) ³		
According to International Patent Classification (IPC) or to both National Classification and IPC		
INT. CL. CO8L 27/06; CO8L 29/06; CO8L 33/02		
U.S. CL. 260/29.6		
II. FIELDS SEARCHED		
Minimum Documentation Searched ⁴		
Classification System	Classification Symbols	
US	260/29.6H, 260/29.6TA, 260/29.6HN, 260/23EM.	
Documentation Searched other than Minimum Documentation to the extent that such Documents are included in the Fields Searched ⁶		
III. DOCUMENTS CONSIDERED TO BE RELEVANT ¹⁴		
Category ⁵	Citation of Document, ¹⁵ with indication, where appropriate, of the relevant passages ¹⁷	Relevant to Claim No. ¹⁸
X	US, A, 3,284,393 PUBLISHED 08 NOVEMBER 1966 VANDERHOFF ET AL	1-9
X	US, A, 4,022,731 PUBLISHED 10 MAY 1977 SCHMITT	1-9
X	US, A, 4,022,736 PUBLISHED 10 MAY 1977 SCHMITT	1-9
X	US, A, 4,077,930 PUBLISHED 07 MARCH 1978 LIM ET AL	1-9
X	US, A, 4,147,681 PUBLISHED 03 APRIL 1979 LIM ET AL	1-9
<p>¹⁹ Special categories of cited documents: ¹⁵</p> <p>"A" document defining the general state of the art</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document cited for special reason other than those referred to in the other categories</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but on or after the priority date claimed</p> <p>"T" later document published on or after the international filing date or priority date and not in conflict with the application, but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance</p>		
IV. CERTIFICATION		
Date of the Actual Completion of the International Search ¹	Date of Mailing of this International Search Report ²	
2 SEPTEMBER 1980	30 JAN 1981	
International Searching Authority ¹	Signature of Authorized Officer ¹	
ISA/US	HAROLD D. ANDERSON	

SUPPLEMENTAL

INTERNATIONAL SEARCH REPORT

International Application No PCT/US80/01352

I. CLASSIFICATION OF SUBJECT MATTER (If several classification symbols apply, indicate all) *		
According to International Patent Classification (IPC) or to both National Classification and IPC		
INT. CL. ³ C08F 2/32		
US CL. 526/207		
II. FIELDS SEARCHED		
Minimum Documentation Searched *		
Classification System	Classification Symbols	
US	526/207	
Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched *		
III. DOCUMENTS CONSIDERED TO BE RELEVANT ¹⁴		
Category *	Citation of Document, ¹⁶ with indication, where appropriate, of the relevant passages ¹⁷	Relevant to Claim No. ¹⁸
X	US, A, 3,457,230, PUBLISHED 22 JULY 1969 KEKISH	10-12
X	US, A, 3,624,036, PUBLISHED 30 NOVEMBER 1971, KEKISH	10-12
X	US, A, 3,957,739, PUBLISHED 18 MAY 1976 CABESTANY ET AL	10-12
X	US, A, 3,975,341, PUBLISHED 17 AUGUST 1976 TRAPASSO	10-12
X	US, A, 4,037,040, PUBLISHED 19 JULY 1977 TRAPASSO ET AL	10-12
X	US, A, 4,078,133, PUBLISHED 07 MARCH 1978 OZIMA	10-12
X	US, A, 4,164,613, PUBLISHED 14 AUGUST 1979 Hoene et al	10-12
<p>* Special categories of cited documents: ¹⁵</p> <p>"A" document defining the general state of the art</p> <p>"E" earlier document but published on or after the International filing date</p> <p>"L" document cited for special reason other than those referred to in the other categories</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the International filing date but on or after the priority date claimed</p> <p>"T" later document published on or after the International filing date or priority date and not in conflict with the application, but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance</p>		
IV. CERTIFICATION		
Date of the Actual Completion of the International Search *	Date of Mailing of this International Search Report *	
18 FEBRUARY 1981	04 MAR 1981	
International Searching Authority *	Signature of Authorized Officer ²⁰	
ISA/US	 HAROLD D. ANDERSON	

FURTHER INFORMATION CONTINUED FROM THE SECOND SHEET

V. ☐ OBSERVATIONS WHERE CERTAIN CLAIMS WERE FOUND UNSEARCHABLE ¹⁰

This international search report has not been established in respect of certain claims under Article 17(2) (a) for the following reasons:

1. ☐ Claim numbers _____, because they relate to subject matter ¹² not required to be searched by this Authority, namely:

2. ☐ Claim numbers _____, because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out ¹³, specifically:

VI. ☒ OBSERVATIONS WHERE UNITY OF INVENTION IS LACKING ¹¹

This International Searching Authority found multiple inventions in this international application as follows:

I. PRODUCT: CLAIMS 1-9	V. PROCESS: CLAIM 15
II. PROCESS: CLAIMS 10-12	VI. PROCESS: CLAIM 16
III. PROCESS: CLAIM 13	
IV. PROCESS: CLAIM 14	

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims of the international application.

2. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims of the international application for which fees were paid, specifically claims:

3. ☒ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claim numbers:

1-9

Remark on Protest:

- ☐ The additional search fees were accompanied by applicant's protest.
☐ No protest accompanied the payment of additional search fees.

FURTHER INFORMATION CONTINUED FROM THE SECOND SHEET

V. ☐ OBSERVATIONS WHERE CERTAIN CLAIMS WERE FOUND UNSEARCHABLE ¹⁰

This international search report has not been established in respect of certain claims under Article 17(2) (a) for the following reasons:

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VI. ☒ OBSERVATIONS WHERE UNITY OF INVENTION IS LACKING ¹¹

This International Searching Authority found multiple inventions in this international application as follows:

- | | |
|---------------------------|-----------------------|
| I. Product: Claims 1-9 | V. Process: Claim 15 |
| II. Process: Claims 10-12 | VI. Process: Claim 16 |
| III. Process: Claim 13 | |
| IV. Process: Claim 14 | |

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims of the international application.

2. ☒ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims of the international application for which fees were paid, specifically claims: 10-12

3. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claim numbers:

Remark on Protest

- ☐ The additional search fees were accompanied by applicant's protest.
- ☐ No protest accompanied the payment of additional search fees.